

(19)



Europäisches Patentamt
European Patent Office
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(11) Publication number:

0 034 881
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 81300294.6

(51) Int. Cl.³: C 09 D 11/00
B 41 M 7/00

(22) Date of filing: 22.01.81

(30) Priority: 28.01.80 US 115916

(43) Date of publication of application:
02.09.81 Bulletin 81/35

(64) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

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(54) Opaque jet ink composition and method.

(57) A novel method of jet ink printing to produce opaque images includes jet ink printing a surface with novel non-opaque jet ink composition, and contacting the printing with a resin opacifying solvent before the ink composition has dried, to render the image opaque. The surface to be printed may be wetted with the resin opacifying solvent before printing or that solvent may be sprayed on the printing.

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OPAQUE JET INK COMPOSITION AND METHOD

The present invention relates to a method of producing opaque printing utilizing a jet ink printer. More particularly the present invention relates to a method of rendering a nonaqueous non-opaque jet ink opaque after it has been printed on a substrate which does not absorb the ink, usually glass or a clear plastic.

Numerous jet inks are known in the prior art, as are various methods of the application of jet ink to produce recorded information. Generally, two major problems arise in the production of inks of commercial value. The first is a problem of settling which arises when the jet printing ink is stored. Most commercially available jet ink printers have nozzle diameters of less than about 125 microns and thus, due to the settling of the pigments contained in the ink, tend to become clogged very easily when the printer is used after being shut down. This type of problem especially arises when pigmented ink is used, since pigments are not soluble in the ink compositions. Further, in order for a jet ink printer to operate satisfactorily, the viscosity of the ink preferably should be less than about 10 centipoise at room temperature. This low viscosity presents problems when the ink contains suspended pigments, as they do not stay suspended over long periods of time,

and thus storage or shelf life is limited. In order to overcome these problems the printer can be modified by increasing the nozzle diameter, adding agitators, or other steps. However, generally, these modifications do not completely solve the problems. Thus, it
5 would be appropriate to be able to provide a jet ink that does not necessarily contain a pigment or dye and yet is still visible upon completion of the printing process.

The process of the present invention, in its most general form, includes printing on a uniform substrate with a conventional
10 jet ink printer, followed by contacting of the printed surface with an opacifying solvent and conventional drying of the opaque jet printed image. While the process of the present invention is particularly suited for transparent and translucent surfaces, such as glass and plastic bottles, it is also suitable for printing on
15 most surfaces which do not absorb ink during jet printing. The invention is most particularly suited for jet printing on glass containers where the opacifying renders the image more visible. The remainder of the process of the present invention will be defined in terms of printing on a glass beverage container, although it is to
20 be understood that it is equally applicable to other surfaces, such as signs, glass and plastic containers, and especially in any circumstance where good image visibility is needed or where adhesion of the printing presents a problem.

The process of the present invention is applicable to all
25 jet ink processes, but in its preferred form the process utilizes jet ink printing with epoxy/phenol resins either alone or in combination with cellulosic resins, since it has been found that these resins print quite well, exhibit good adhesion to the preferred glass and plastic surfaces, and are surprisingly

opacifiable by the process described herein. In this case, the preferred opacifying solvent is an aqueous soap solution. Additionally, when modified rosins, polyketones, or polyamids are utilized the opacifying solvent does not necessarily contain soap,
5 and thus may be water.

In the preferred form of the process of the present invention, the substrate surface is contacted or wetted with the opacifying solvent, by for instance spraying, misting, or dipping in a bath, and, while the substrate surface is uniformly moist or damp,
10 it is jet ink printed. The initial opacifying solvent contact step is effected to provide a uniform printing surface as well as to provide further opacifying capabilities to the present process. It may be eliminated if the surface that is to be printed is uniform in character, and if good wetting and adhesion of the jet ink can be
15 obtained. However, prespraying is preferred since the opacity of the product is increased when the step is utilized. The jet ink printing is effected with standard ink compositions, including, if desired, a dye or other colorant. However, the dye is not a necessary component as the inks are rendered opaque by the process
20 of the present invention, and thus are visible.

The inks, in their preferred form, constitute another portion of the present invention. It has been found that the process of the present invention, and, in fact, all jet ink printing processes, are significantly improved by the addition of a slow
25 evaporating solvent to the ink. The slow evaporating solvent is a heterocyclic organic compound, defined hereinbelow, and improves the wetting and printing characteristics of the ink and, in addition, aids in maintaining the ink in a sufficiently wet condition to allow for the final application of the opacifying solvent which renders

the printed ink opaque.

After printing by standard methods, and before the ink has dried, the printed item is subjected to the opacifying solvent a second time by, e.g., spraying, misting, immersion or vapor contacting. The time lag between printing and opacifying depends upon the ink composition, and the particular resin utilized. For instance, where a high solids ink is utilized, and the slow evaporating solvent is not present in the ink, then the opacifying solvent must be applied almost immediately after printing. However, if a lower solids ink composition and the slow evaporating solvent are used, then the time lag between printing and application of the opacifying solvent may be increased. Also, the temperature and the type of resin would affect the amount of time that the opacifying solvent must be maintained in contact with the printed article. Preferably, the opacifying solvent is applied by a mist or spray, especially when the time lag between printing and solvent contact is quite small. In the alternative, if the particular resin does not easily opacify, then it would be appropriate to dip the articles in a bath of the opacifying solvent, or spray them for a lengthy period of time, for instance, while they travel on a conveyor. These steps can be effected in ordinary bottle handling processes by the inclusion of art-recognized apparatus.

The inks utilizable in the process of the present invention have viscosities of from about 0.5 to 25 cps at 25°C, preferably from about 1.35 to 4.0 cps at 25°C. However, slight variations in viscosity do occur due to evaporation and settling effects during processing, and especially after the solution is allowed to sit for a lengthy period of time, i.e. during overnight shutdowns. Thus, the viscosity ranges for the inks need to be adjusted during operation

so that the jet printer properly forms the droplets necessary for jet printing. It should be further pointed out that since the rate of droplet formation, i.e. up to about 150,000 droplets per second, is determined by the orifice size in the piezoelectric crystal, and since the droplet size determines the signal input required to deflect the droplets, the viscosity of the solution is quite important. In addition, in view of the fact that jet printers utilize electrostatic field deflection of the droplets, the resistivity of the solution is important. For the process of the present invention the resistivity may be as high as 10,000 ohms-cm., but is preferably in the range from about 250 to 3,000 ohm-cm.

Numerous resins are utilizable in the process of the present invention, and, in general, the total resin content of the solution is from 2 to 60% by weight, and, preferably, from about 10 to about 25% by weight. The total resin concentration can be divided into two separate groups, as one of the optional features of the present invention is the use of a cellulosic resin. When present, the cellulosic resin would be utilized in amounts up to about 15% by weight, preferably from about 1 to 5% by weight, and the non-cellulosic resins would be present in a range of from 2 to 50% by weight, preferably from about 9 to about 20% by weight, all based on the total solution weight.

The resins utilizable in the ink compositions of the present invention are individual resins and mixtures of resins, utilizable in jet printing operations. These include the polyester resins, epoxy/phenolic resin mixtures, rosins and modified rosins, particularly pentaerythritol modified rosins, polyketones, and polyamids. With regard to the cellulosic component, modified celluloses are utilized. The preferred modified celluloses include

nitrocelluloses, alkylcelluloses, particularly ethylcellulose, and cellulose esters such as cellulose acetate and cellulose acetate butyrate. The particular resins chosen depends on the particular use desired. It has been found that all of the above resins can be
5 opacified to at least some degree. However, the modified rosins, and the ketone-based resins exhibit very good opacity when applied to addition polymer substrates such as polyethylene and thus are preferred for this use. The epoxy/phenolic resins on the other hand were found to operate surprisingly well on glass bottles, and it was
10 further found that when the epoxy/phenolic resins were combined with a cellulose derivative, the resulting printing on wet glass bottles exhibited the best opacity and adhesion.

The solvents utilized for the resin are generally aliphatic alcohols, ketones, and hydrocarbons. These are known in the art and
15 include, in the best mode, mixtures of a lower aliphatic alcohol, i.e. an alcohol having 1 to 6 carbon atoms such as methanol or ethanol, and a lower aliphatic ketone, i.e. ketones with from 1 to 8 carbon atoms such as acetone or methyl ethyl ketone. In this form the lower aliphatic alcohol and the ketone are each present in a
20 range from about 20% to about 80%. In the most preferred form the alcohol and ketone percentages each vary from 40% to 60% by weight, based on the solvent mixture. The solvent concentration in the solutions ranges from about 40% to 98% of the total ink composition, and preferably from about 50% to about 81% by weight of the total
25 ink composition.

In order to provide good printing characteristics, electrolytes are normally added to the solution. The electrolytes include inorganic acids and short chain aliphatic carboxylic acids, i.e. acids containing from 1 to 3 carbon atoms and the salts of such

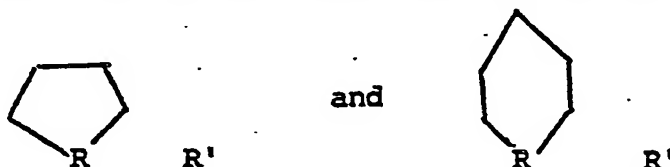
acids, including, but not limited to, chlorides, sulfates, nitrates, formates, acetates, and other salts. The salts may be formed from alkali metals and alkaline earth elements, as well as ammonia. In addition, substituted sulfonic acids, such as para-toluene sulfonic acid etc. may be utilized as the electrolyte. It has been found that halide salts are most useful with the modified rosins, that para toluene sulfonic acid, and its derivatives are most useful with the modified rosins, particularly with pentaerythritol modified rosin. Lastly, it has been found that ammonium formate is the preferred electrolyte for use in epoxy/phenolic resin containing inks, especially those where the ink includes a cellulose derivative. The electrolytes are present in a range from about 0 to about 5% by weight, preferably about 0.1% to about 1.5% by weight.

Additionally, dyes or coloring materials may be provided in the ink compositions utilized in the present invention; however, such dyes and coloring materials are not necessary since the present process renders the ink opaque. When the dye is present, it is usually included in an amount up to about 10% of the total weight of the solution, preferably from about 0.1% to about 2.0% by weight. The dyes are basic dyes which are soluble in the particular solvent selected for the ink. By basic dyes, it is meant dyes which, in solution, have a pH of greater than 7.0. Exemplary dyes include Auramine Base NS, Rhodamine Base FB, Victoria Blue Base FB, and Methyl Violet Base FB.

Since many dyes act as electrolytes, the need for an electrolyte component depends on the dye selected. Also, since the resultant printed image is opaque, dyes are also optional. However, in order to obtain good printing characteristics, at least one of the two should be included. That is, either a dye, an electrolyte

or both are to be present in the ink. The selection of these two components is usually controlled by the need for the ink to exhibit the above described physical characteristics.

In an additional form of the present invention, the inks
5 contain from about 0 to 40% by weight, preferable from about 7.5% to 30% by weight of a slow evaporating solvent. Slow evaporating solvents are those which exhibit a lower vapor pressure than the other solvents contained in the ink composition. These solvents are saturated and unsaturated heterocyclic compounds having five or six
10 membered rings, which may be side chain substituted, and include lactones, amids, and amines being defined by the formulae:



15

wherein R is a divalent oxygen or nitrogen radical, R' is hydrogen, divalent oxygen, hydroxyl, alkyl of from 1 to 5 carbon atoms, oxyalkyl of from 1 to 5 carbon atoms, monovalent ammonium, or a halogen radical. As noted, the ring may be either saturated or
20 unsaturated, depending on the material chosen. Additionally, the rings may have up to 3 hetero atoms including oxygen, nitrogen and combinations thereof. The particular preferred slow evaporating solvents are butyrolactone, caprolactone, and pyrrole. Additionally, the heterocyclic ring may contain plural, i.e. up to
25 3, heteroatoms. The slow evaporating solvents in all cases, though, must be soluble in the ink and especially in the other solvents. Usually these solvents have a vapor pressure of under 10 mm Hg., preferably about 2 to 3 mm Hg., at standard temperature and pressure.

The opacifying solvent is usually water, or a water solution, preferably a soap solution. However, the opacifying solvent may be an aqueous solution of a commercially available wetting agent. The limitations found below are applicable to such agents in order to render the resultant images opaque. Soap, as used in the present application, is defined as saponified or partially saponified fatty acids and glycerides and their salts, such as sodium stearate. The pH of the water is adjusted by normal means, if needed, such as by the addition of small amounts of hydrochloric acid or sodium hydroxide, so that it usually has a pH in the range of 3 to 10, preferably in the range of 6 to 8. Any pH adjustment that is needed is preferably done with a material compatible with the electrolyte utilized in the ink composition. Additionally, although water is the preferred opacifying solvent, organic and inorganic liquids that are miscible with the ink solvent and immiscible with the solids may be used. These opacifying solvents must be selected to have the effect of drawing the solvent from the ink and thus taking the resin in the ink out of solution before it dries. The result is that the resin in the ink is rendered opaque either from its dissolution or from the inclusion of small amounts of opacifying solvent in the ink as it dries. The opacifying solvent, in order to provide the needed coating action to opacify the ink, should, in addition, have a surface tension of about 72 dyne-cm or less, preferably about 40 dyne-cm or less.

A better understanding of the present invention may be had from a consideration of the following examples; however, the examples are not to be construed as limiting, as they are illustrative of the preferred forms of the present invention, and not a definitive list of compositions. In all of the examples

listed below, all of the formulations are on a total ink solution weight basis, unless otherwise indicated.

Example 1

Nine inks were prepared in accordance with the formulas indicated in Table I. In each case, the ink was printed on a glass base, and thereafter subjected to a water spray before drying. In each case, the ink functioned quite well, and turned opaque upon the water treatment. The water had a pH of 7.5. Inks 1A to 1F were treated with a soap solution containing a 2% concentration of soap and having a surface tension of about 30.

TABLE I

INK FORMULATIONS

	Ink 1A	Ink 1B	Ink 1C	Ink 1D	Ink 1E	Ink 1F	Ink 1G	Ink 1H	Ink 1J
Resin A*	3.20								
Resin B*		4.00							
Resin C*	9.60	12.00							
Resin D*									2.70
Resin E*			15.00						
Resin F*						2.50			
Resin G*				9.60					
Resin H*					9.90				
Nitrocellulose	3.20	4.00	2.00	3.30	1.50	6.00	3.20		
Ethyl Cellulose						1.50	1.30		
Cellulose Acetate								6.15	
Butyrate									
Methanol	27.00	22.10	39.00	31.10	32.60	78.50	95.37	81.85	52.25
Isopropyl Alcohol						5.50			
Methyl Ethyl Ketone	27.00	42.00	19.00	31.00	32.40	5.00		11.60	21.25
Acetone									22.30
Butyrolactone	28.70	15.50	23.00	21.00	20.00				
Ammonium Formate	0.30	0.40		0.40	0.30	1.00			
Para-Toluene Sulphonic Acid								0.13	0.40
Auramine Base NS			2.00						
Rhodamine Base FB	1.00								
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

*Resin A is D.E.R. 662, an epoxy resin produced by the Dow Chemical Company havin and epoxide equivalent weight of 575 to 700, a softening point of 80 to 90°C. using Durran's Mercury Method, and a Gardner-Holdt viscosity of H-L in a 40% weight solution of a glycol ether. The color index is a maximum of 1 using the Gardner color standard of 1933.

*Resin B is EPON 1001, a Shell Chemicals epoxy resin exhibiting a Gardner-Holdt viscosity of D-G, a viscosity of from 1.0 to 1.7 (using ASTM test D-445), and exhibiting an epoxide equivalent of from 450 to 550, with a maximum Gardner color of 4.

*Resin C is AROFENE 6530 an Ashland Chemicals phenolic resin exhibiting a Gardner-Holdt viscosity at 25° of D-K (50% solution in denatured ethanol), a softening point of 180 to 210°F., using the Dennis Bar Method, a Gardner maximum color of 12 (using a 50% solution in denatured ethanol). The resin is a 100% phenol-formaldehyde thermoset.

*Resin D is ACRYLOID B-66 produced by Rohm and Haas comprising a polymerized mixture of acrylic acid, methacrylic acid and their esters.

*Resin E is PENTALYN 255, produced by Hercules, and is a rosin derived thermoplastic resin having an acid number of 180 to 200, a Gardner-Holdt viscosity at 25°C., of at least G, and a maximum Gardner color of 7, both in a 60% solids solution in ethanol.

*Resin F is KRUMBHAR 1717 HMP produced by the Krumbhar Resin Division of Lawter Chemicals Inc. It is a ketone based synthetic resin exhibiting a Gardner (1933) color of 2+ in a 60% isopropanol solution.

*Resin G is EMEREX 1511 produced by Emery Chemicals, and is a linear polyamide resin produced by condensation of fatty acids with

polyalkyl polyamines. The resins have an amine value of 230 to 246 in hypochloride, a kinematic of viscosity of 31 to 38 poise at 75°C., a maximum Gardner color of 9.

*Resin H is VE 307 POLYESTER produced by Goodyear Rubber Company, exhibiting an extrinsic viscosity of 0.77, and an acid number of greater than 5.

The cellulose acetate butyrate utilized was supplied by Eastman Chemical Products Inc., and had an average weight percent butyryl content of 47, and an acetyl content of 2.0 and a hydroxyl content of 4.7. The hydroxyl equivalent weight was 362.

It should be noted that inks 1A through 1E utilized butyrolactone in combination with methanol and methyl ethyl ketone as a solvent system. In this system, the heterocyclic lactone performed quite well and resulted in good opacity being obtainable by the process of the present invention. In addition, the inks adhered well to the glass substrates utilized in all of the cases.

Example 2

A second series of tests was run using other resins, and substituting magnesium chloride as the electrolyte, as well as utilizing a dye. In each of these cases, good adhesion was obtained in the jet printing process, and the desired opacity was produced by the subsequent spraying of water onto the surface of the printed substrate, prior to the drying of the ink.

The compositions utilized are indicated in Table II herein.

TABLE II

	Ink A	Ink B	Ink C
Resin J*	2.90		
Resin K*		2.60	
5 Resin L*			3.75
Ethyl Cellulose	1.20	1.10	1.40
Methanol	11.90	10.40	13.30
Methyl Ethyl Ketone	64.95	70.10	62.10
Methyl Cellusolve	18.50	15.25	19.30
10 Magnesium Chloride	0.15	0.15	0.20
Auramine Base NS	0.40	0.40	0.40
Total Weight	100.00	100.00	100.00

*Resin J is 100% phenolic resin produced by Ashland Chemicals
15 under the name or Arofen 669 exhibiting a Gardner-Holdt viscosity
of 1.5 to 2.5 when in a 60% solution in toluol and maximum Gardner
color of 4.

*Resin K the Arofen 85678 an Ashland Chemicals 100% phenol
formaldehyde thermosetting resin exhibiting a Gardner-Holdt
20 viscosity at 25°C. of H-N, a softening point (using the Dennis Bar
Method) of 77 to 93°C., and a maximum Gardner color (1963) of 12
(50% solution in denatured ethanol).

*Resin L is RCI 29419 of RCI Chemicals having a softening point
(ball and ring) of 105 to 120°C. It is a thermosetting phenolic
25 resin.

Example 3

Other inks were prepared utilizing phenolic resins, individually and in mixtures, and utilizing butyrolactone as the slow evaporating solvent in some cases for comparison. Dyes were added to seven of the eight compositions. In each case the coatings
5 on glass containers were produced by jet printing, and a soap solution containing 2% soap solution in water was utilized to opacify the printed inks. In this case, the glass bottles were wet prior to the application of the ink, and still adherence of the ink was quite good, and the opacity was very good. The particular ink
10 compositions utilized are shown in Table III.

*Resin M is DER 661, produced by Dow Chemicals, and is an epoxy resin. It has an epoxide equivalent weight of 475 to 575, a softening point (Durran's Mercury Method) of 70 to 80°C., a Gardner-Holdt viscosity of G-J and a Gardner maximum color of 1.

5 *Resin N is aroclene 24870 produced by Ashland Chemicals, and is a 100% phenol formaldehyde thermoset of the bisphenol type. It has a Dennis Bar softening point 175 to 205°F., and a Gardner-Holdt viscosity (60% solution in denatured ethanol) at 25° of K-U, and a Gardner (1963) maximum color of 11 (60% resin in ethanol).

10 Example 4

In order to test the various heterocyclic slow evaporating solvents, several tests were run utilizing different slow evaporating solvents. The ink compositions in all cases were epoxy/phenol resin mixtures, in combination with ethyl cellulose, the preferred form of
15 the ink resin composition. The only variable utilized was that a different heterocyclic slow evaporating solvent was used in each case. In all cases, the ink printed quite well, and when subjected to a soap solution after printing, and before drying, the printing became opaque and quite visible. The compositions of the inks
20 utilized for this test are shown in Table IV.

TABLE IV

	Ink 4A	Ink 4B	Ink 4C
Resin M	3.50	3.50	3.50
Resin O*	10.50	10.50	10.50
5 Ethyl Cellulose	1.50	1.50	1.50
Methanol	34.70	34.70	34.70
Methyl Ethyl Ketone	34.50	34.50	34.50
Butyrolactone	15.00		
Caprolactone		15.00	
10 M-Pyrol			15.00
Ammonium Formate	.30	.30	.30
	100.00	100.00	100.00

*Resin O is Aroclene 6530 produced by Ashland Chemicals, which is
 15 a 100% phenol-formaldehyde thermosetting resin. The resin exhibits
 a Dennis Bar softening point of 180 to 210°F., and a Gardner-Holdt
 viscosity of D-K at 25°C. (50% solution in denatured ethanol). The
 Gardner color (1963) is a maximum of 12 (in the same ethanol
 solution).

20

Example 5

Several other ink compositions were prepared utilizing no
 cellulosic resin. In each of these cases, the same procedures were
 followed, and in each case, good printing and good opacity were
 obtained by the use of a soap solution as before. However, in this
 25 case the opacity was not quite as good as the epoxy/phenol mixture
 in combination with a cellulosic resin.

TABLE V

	Ink 5A	Ink 5B	Ink 5C
Resin M	3.35	4.00	3.50
Resin O			10.50
5 Resin N	10.10		
Resin G		8.00	
Methanol	44.80	32.30	35.00
Methyl Ethyl Ketone	28.00	30.30	25.70
Methyl Cellusolve	12.35	25.00	
10 Butyrolactone			25.00
Magnesium Chloride	0.30		
Ammonium Formate		0.40	0.30
Rhodhamine Base FB	1.10		
	100.00	100.00	100.00

CLAIMS:

1. A non-opaque jet ink composition comprising:
from 2% to 60% by weight of a resin or mixture thereof;
from about 40% to about 90% of a resin solvent selected
from the group consisting of aliphatic alcohols, ketones,
5 hydrocarbons, and mixtures thereof;
from about 0% to about 5% of an electrolyte;
up to about 10% of a dye or other coloring material;
and
up to about 40% of a slow evaporating solvent selected
10 from the group consisting of substituted and unsubstituted
heterocyclic compounds having 5 or 6 membered rings and from 1 to 3
oxygen or nitrogen atoms in the ring,
said ink exhibiting a viscosity of from 0.5 to 25 cp. at
25°C. and having a resistivity of up to 10,000 ohm-cm.
15
2. The composition of claim 1 wherein the resin is a
mixture of from 2% to 50% of a first resin, and from 0% to 15% of a
second resin which is a modified cellulose selected from the group
consisting of cellulose esters, alkyl celluloses, and cellulose
20 nitrates.
3. The composition of claim 1 or claim 2 wherein the resin
concentration is from about 9 to about 20%, and the modified
cellulose concentration is from about 1 to about 5% by weight.
25
4. The composition of any of claims 1 to 3 wherein the
first resin is an epoxy/phenol type resin.

5. The composition of any of claims 1 to 4 wherein the resin solvent is present in an amount of from 50% to 81% by weight of the total ink and is a mixture of a lower aliphatic alcohol or a lower aliphatic ketone, each containing from 1 to 6 carbon atoms.

5

6. The composition of claim 5 wherein each of the resin solvent is present in the solvent mix in an amount of from about 20% to 80% by weight.

10

7. The composition of any of claims 1 to 6 wherein the resin solvent mixture contains from about 40% to about 60% by weight of each solvent.

8. The composition of any of claims 1 to 7 wherein the
15 electrolyte is selected from the group consisting of alkali metal, alkaline earth, and ammonium salts of inorganic acids and short chain aliphatic carboxylic acids.

9. The composition of any of claims 1 to 8 wherein the
20 electrolyte is present in an amount from about 0.1% to about 1.5% by weight and is a chloride, a nitrate or a sulfate salt.

10. The composition of any of claims 1 to 9 wherein the dye is present in an amount of from 0.1% to about 2% by weight.

25

11. The composition of any of claims 1 to 10 wherein the slow evaporating solvent is present in an amount from about 7.5% to about 30% by weight and is selected from the group consisting of

lactones and cyclic inner amids and cyclic inner amines.

12. The composition of any of claims 1 to 11 wherein the slow evaporating solvent is selected from the group consisting of
5 butyrolactone, and caprolactone.

13. The composition of any of claims 1 to 12 wherein the slow evaporating solvent has a vapor pressure of less than 10 mm. Hg. at standard temperature and pressure.

10

14. The composition of claim 13 wherein the vapor pressure is from 2 to 3 mm. Hg.

15. The composition of claim 1 wherein the viscosity of the
15 ink is from 1.35 to 4 cp., and the resistivity is from about 250 to about 3,000 ohm-cm.

16. A method of producing opaque indicia by jet ink printing utilizing the jet ink composition specified in any of
20 claims 1 to 15, the method comprising the steps of:

forming a jet of discrete droplets of said ink and directing and modulating said jet toward a uniform printable substrate to form printed information thereon;

while said printed information is still wet, applying
25 thereto a coating of an opacifying solvent miscibles with the resin solvent and slow evaporating solvent in said ink composition but immiscible with the resins in said ink composition; and

drying the thus opacified printed information.

17. The process of claim 16 wherein the opacifying solvent is applied to the substrate prior to printing in the form of a uniform thin layer.

5 18. The process of claim 16 or claim 17 wherein the opacifying solvent is applied to the printed substrate by spraying.

19. The process of any of claims 16 to 18 wherein the opacifying solvent is selected from the group consisting of water
10 and aqueous soap solutions.

20. The process of any of claims 16 to 19 wherein the pH of the opacifying solvent is from 3 to 10.

15 21. The process of any of claims 16 to 20 wherein the solvent pH is from 6 to 8.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
P	<u>FR - A - 2 385 782 (M & T)</u> * Page 13, claims 1,2; page 14, claims 8 and 11 *	1,8	C 09 D 11/00 B 41 M 7/00
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	<u>GB - A - 2 004 904 (M & T)</u> * Abstract *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.) C 09 D 11/00 B 41 M 7/00
	--		
	<u>US - A - 4 168 254 (DAVID A. FELL)</u> * Column 8, claims 1 and 2 *	1	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	--		
	<u>GB - A - 2 030 075 (WHITTAKER)</u> * Page 4, claim 3; page 1, lines 96-103 and 120-125 *	1,15,16,19	&: member of the same patent family, corresponding document

b The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 10-06-1981	Examiner GIRARD

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- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
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